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Dielectric and Piezoelectric Properties of a Triple Ferroceramics System $PbTiO_3$-$PbZrO_3$-$Pb(Mn_{1/3}Nb_{2/3})O_3$

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Abstract. The article is a study of dielectric and piezoelectric properties of six compositions of PZT-ceramics with an addition of $Pb(Mn_{1/3}Nb_{2/3})O_3$. In the case of concentration of the additive of 0.05 mol, the dielectric and piezoelectric parameters are as follows: $\varepsilon_r = 875$, $Q_M = 2030$, $\tan\delta = 0.34\%$, $K_p = 0.45$, $d_{31} = 90 \times 10^{-12}\mathrm{C\,N^{-1}}$. Within the temperature interval from -30°C to 50°C, the frequency independent parameter N_r changes by about 0.6%.

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1 Introduction

The modified $Pb(Zr,Ti)O_3$ ceramics is currently the most widely used in the preparation of piezoceramic components [1-8]. The requirements to the input materials vary depending on the intended use of these piezocomponents. The purpose of the present study is to establish a material suitable for the production of piezoelectric transformers and ultrasonic generators and receivers. They operate using the double transformation of energy – the electrical energy at the inlet is transformed into mechanical resonance oscillations, and at the outlet the mechanical energy is transformed into an electric signal. The efficiency of energy transformation is typified by the coefficient of electromechanical connection K_{ij}. Together with the high K_{ij}, the materials should have low dielectric and mechanical losses as they cause heating of the piezocomponents.

The energy transformation coefficient in an idle run regime of the transverse-transverse piezotransformers is defined by the equation [9,10]:

$$K_{uo} = \frac{4K_{31}^2 Q_M}{\pi(1 - K_{31})}$$

where Q_M is the mechanical quality factor, and K_{31} is the electromechanical connection coefficient.

The maximum coefficient of efficiency of transverse-longitudinal piezotransformers is defined by the equation [10]:

$$\eta_m = \frac{2K_{33}^2 Q_M}{2K_{33}^2 Q_M + \pi^2}.$$

The two formulae reveal that the $Q_M K_{ij}^2$ could be used as a common parameter of the material.

The dielectric losses $\tan\delta$ are a major factor limiting the efficiency coefficient η_m. That is why another important parameter to be considered is the ratio $K_{jj}^2/\tan\delta$.

Besides K_{ij}, Q$_M$, and $\tan\delta$, other parameters influencing the efficiency of piezotransformers are d_{31} and d_{33}, as well as the dielectric constant ε_r.

2 Experimental Procedure

The studied samples were made by using a standard ceramics technology. The input materials were PbO, ZrO_2, MnO_2, Nb_2O_5 – all with a purity of 99.6%. The measured materials were homogenized for 1 h in a ball mill using distilled water. After being dried, the mixture was baked at a temperature of 900°C for 2 h, granulated and formed as discs. They were strengthened at a temperature of 1220°C in a nickel container for 2 h. The experimental samples were shaped as 0.5 mm-thick discs with a diameter of 6 mm. The electrode used was silver paste baked at a temperature of 800°C. The samples were polarized in silicone oil at a temperature of 100°C and under a constant voltage of 4 kV/mm for 1 h.

The dielectric constants ε and $\varepsilon_{r,}$ and the dielectric losses $\tan\delta$ were defined by means of a RLC-digital bridge at a frequency of 1 kHz. The electromechanical coupling factor K_p, the piezomodule d_{31} and the mechanical quality factor Q_M were defined using the resonance-antiresonance method. Temperature dependence and the frequency invariant N_r were studied in the temperature range from -30°C to 50°C.

3 Results and Discussion

Figure 1 gives the dependence of the dielectric constant ε of the non-polarized samples and the dielectric constant ε_r of the polarized samples in terms of their dependence of the concentration of (Mn$_{1/3}Nb_{2/3}$)O$_3$. Up to about 0.05 mol, the constants grow and after that they slowly and gradually go down. Polarized samples have higher relative dielectric permittivity. The dependence of the dielectric losses $\tan\delta$ on the concentration of the additive is given in Figure 2.

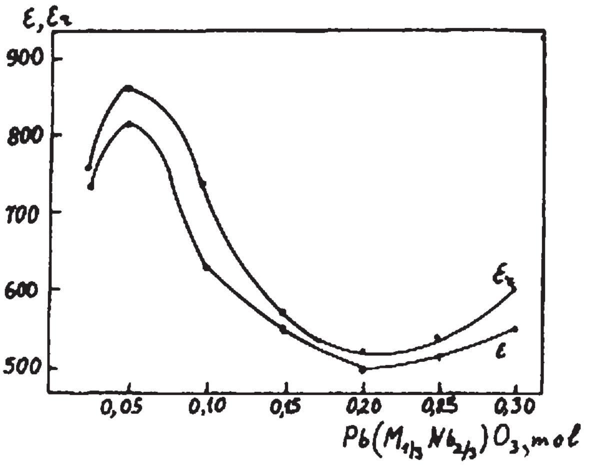

Figure 1. Dependence of dielectric constant of non-polarized samples (ε) and polarized samples (ε_r) on the concentration of $Pb(Mn_{1/3}Nb_{2/3})O_3$

At a concentration higher than 0.075 mol, the materials have abnormally high dielectric loss. Similar results have been observed by Wersing, who studied ceramics modified with manganese only [11]. During the baking of the ceramics, manganese ions accumulate at the borders of the grains and form conductor ar-

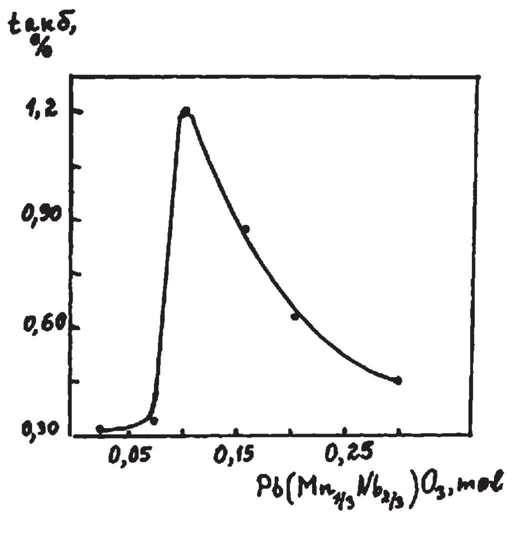

Figure 2. Dependence of the dielectric losses $\tan\delta$ on the concentration of $Pb(Mn_{1/3}Nb_{2/3})O_3$

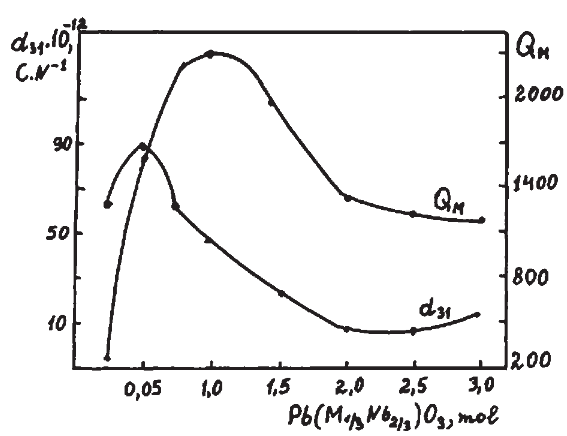

Figure 3. Dependence of the piezomodule d_{31} and the mechanical quality factor Q_M on the concentration of $Pb(Mn_{1/3}Nb_{2/3})$

eas, i.e. the abnormal dielectric losses are caused by the increased conductivity of the samples. Besides, the higher concentration of manganese slows down the growth of the ceramics grains.

Figure 3 shows the dependence of the piezomodule d_{31} and the qualitative factor Q_M on the composition of the materials, and Figure 4 gives the analogous dependencies of the electromechanical coupling factor K_p and the frequency independent parameter N_r. The piezomodules d_{31} and K_p increase up to 0.05 mol

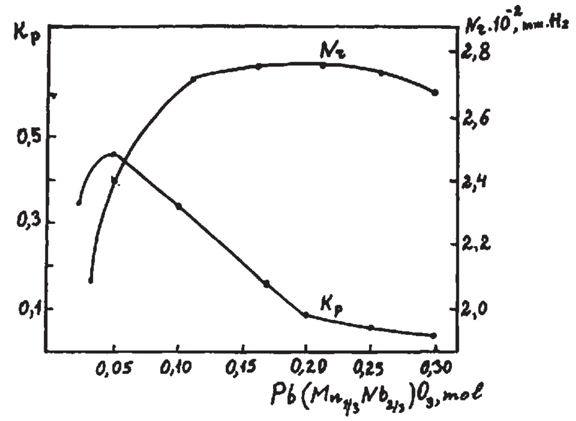

Figure 4. Electro-mechanical coupling factor K_p and the frequency independent parameter N_r versus the concentration of $Pb(Mn_{1/3}Nb_{2/3})O_3$

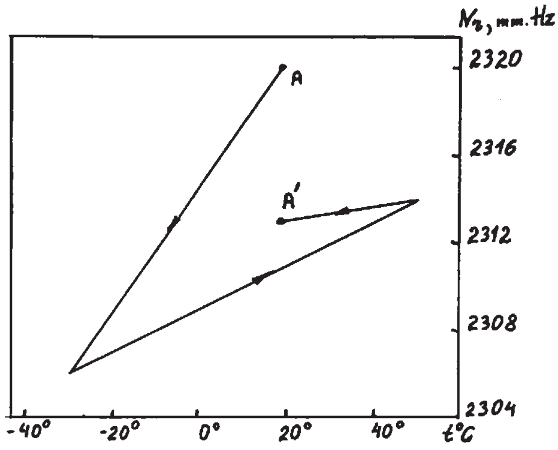

Figure 5. Temperature dependence of the frequency independent N_r of the composition $Pb[Ti_{0.47}Zr_{0.48}(Mn_{1/3}Nb_{2/3})_{0.05}]O_3$

$Pb(Mn_{1/3}Nb_{2/3})O_3$, and then they gradually decrease. The mechanical quality factor Q_M and the frequency independent parameter N_r increase to the concentration of the additive of 0.1 mol and 0.12 mol, respectively. It is important to note that at a concentration of 0.050 mol, where d_{31} and K_p have their maximum values, Q_M is sufficiently high and has a value of about 1600.

Figure 5 shows the temperature dependence of the parameter N_r on the material's composition $Pb[Ti_{0.47}Zr_{0.48}(Mn_{1/3}Nb_{2/3})_{0.05}]O_3$. Within the temperature interval from 50°C to -30°C, N_r changes by about 0.6%, i.e. the material demonstrates a good temperature dependence of the resonance frequency.

The experimental results (Figures 1–4) reveal that depending on concentration, the additive $Pb(Mn_{1/3}Nb_{2/3})O_3$ has a different impact on the ceramics parameters. Up to 0.05 mol, it acts like a 'ferrosoftener' since ε_r, d_{31} and K_p increase. At higher concentrations these parameters decrease, i.e. the ceramics hardens. This effect of the additive is due to the changeable valence of manganese. In the process of synthesis of hard solutions, these actually contain the cations Mn^{2+}, Mn^{3+}, Mn^{4+}. In this sequence the electrical reduction of the cations grows, as does the ferrohardness. Therefore, the conclusion can be drawn that at concentration of the additive higher than 0.05 mol, there is a considerable amount of Mn^{4+} cations. Besides, when substituting the Mn^{3+} for Zr^{4+} in the hard solution, oxygen valences are created. They limit the mobility of domain walls, the coercive field increase, and the dielectric permittivity and the piezo-activity of the materials decreases.

References

[1] S. Priya, H-Woo Kim, K. Uchino (2004) *J. Am. Ceram. Soc.* **87** 1907.

[2] O. Ise, K. Satoh and J. Matiya (1999) *Jpn. J. Appl. Phys.* **38** 5531.

[3] J. Woo, Y. Lee, K. Yoon, S. Hwang, S. Suh, J. Kim and C. Yoo (2001) *Jpn. J. Appl. Phys.* **40** 3256.

[4] M. Nadoliisky, T. Vasileva and P. Vitkov (1992) *Ferroelectrics* **129** 141.

[5] K. Prasad (2000) *Indian J. Eng. Mat. Sci.* **7** 446.

[6] L.X. He, M. Gao, C.E. Li, W.M. Zhu, H.X. Yan (2001) *J. Eur. Ceram. Soc.* **21** 703.

[7] J.W. Long, H.Y. Chen, Z.Y. Meng (2004) *J. Inorg. Mater.* **19** 101.

[8] K. Prasad, R.N.P. Choudhary, R. Sati (1995) *Natl. Acad. Sci. Lett. – India* **18** 145.

[9] V. Lavrinenko (1975) *Piezoelectric Transformer*, Energia, Moscow (in Russian).

[10] I. Kartachov, N. Marchenko (1978) *Piezoelectric Transformer*, Technika, Kiev (in Russian).

[11] W. Wersing (1978) *Ferrelectrics* **22** 813.